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(71) Applicant : KYOCERA CORPORATION  
5-22, Kita Inoue-cho Higashino  
Yamashina-ku Kyoto-shi (JP)

(72) Inventor : Nagato, Yoshio, c/o Kyocera  
Corporation  
1-4, Yamashita-cho  
Kokubu-shi, Kagoshima-ken (JP)  
Inventor : Hamashima, Hiroshi, c/o Kyocera  
Corporation  
1810, Nishi-machi, Takashiro-cho  
Sendai-shi, Kagoshima-ken (JP)

(74) Representative : Alber, Norbert et al  
Albert-Rosshaupter-Strasse 65  
W-8000 München 70 (DE)

(54) Sintered alloy of golden color.

(57) This invention comprises a sintered alloy of a nitride of titanium or a carbonitride of titanium and metals having vivid gold color, being excellent in strength, hardness and anticorrosiveness as well as facilitating for a sharp edge working, wherein titanium is contained in an amount of 55 to 75% by weight with respect to the whole amount, metals of the iron family and elements of the Group 6a of periodic table including at least chromium are contained in an amount of 3 to 30% by weight with respect to the whole amount, and the remainder being non-metallic elements consisting of nitrogen or nitrogen and carbon, and wherein the ratio of carbon with respect to said non-metallic elements is smaller than 10% by weight, and the ratio of chromium in the metal elements excluding titanium is not smaller than 35% by weight.

EP 0 520 465 A1

## BACKGROUND OF THE INVENTION

The present invention relates to a sintered alloy which exhibits gold color and is used for ornamental purposes.

5 As materials for ornamental purposes exhibiting gold color, there have heretofore been used a variety of metals such as pure gold, alloys thereof, brass and the like, as well as those metals of which the surfaces are plated with gold. However, these metals all have small hardnesses and get scratched on the surfaces or cracked when they come into contact with hard substances. In order to prevent the surfaces from being scratched, further-  
10 more, a variety of metals have been coated with hard layers that exhibit gold color. However, these layers have different properties and tend to be peeled off because of their insufficient strength.

In order to overcome the above-mentioned defects in recent years, therefore, there have been used in many cases sintered alloys of gold color obtained by bonding a metal such as nickel or cobalt to the nitride of a metal such as titanium nitride (Japanese Laid-Open Patent Publication No. 58335/1990).

15 However, the aforementioned gold-color sintered alloys are usually sintered poorly. In order to improve such sintering property, therefore, the sintering must be carried out by adding various additives such as carbides or carbonitrides of elements of the Groups 4a, 5a and 6a of periodic table.

In fact, however, such additives cause the color tone of the sintered products to greatly change from their gold color into other colors. In particular, when carbides or carbonitrides of elements of the Groups 4a, 5a and 6a of periodic table are added, the color tone of the sintered product changes into a red copper color making  
20 it difficult to obtain a vivid and favorable gold color, though the sintering property is improved.

Furthermore, an increase in the amounts of additives results in a remarkable increase in the dropped-out particles of the sintered product during the grinding and an increase in the voids in the sintered product, causing the strength and hardness to decrease and making it difficult to obtain a mirror surface despite the effort of polishing.

25 Moreover, an increase in the amounts of additives results in a decrease in the corrosion resistance against the human sweat and sea water.

Further, the sintered products exhibit poor anti-chipping property, easily develop dropped-out particles at the time of machining for making ornaments, and make it difficult to carry out sharp-edge machining.

30 The object of the present invention therefore is to provide a sintered alloy of gold color having vivid and favorable gold color tone, high strength and hardness, excellent corrosion resistance, excellent anti-chipping property, and which permits the sharp-edge machining to be easily carried out.

According to the present invention, there is provided a sintered alloy of gold color comprising a nitride of titanium or a carbonitride of titanium and metals, wherein titanium is contained in an amount of 55 to 75% by weight with respect to the whole amount, metals of the iron family and elements of the Group 6a of periodic  
35 table including at least chromium are contained in an amount of 3 to 30% by weight with respect to the whole amount, and the remainder being non-metallic elements consisting of nitrogen or carbon, and wherein the ratio of carbon with respect to said non-metallic elements is not greater than 10% by weight, and the ratio of chromium in the metal elements excluding titanium is not smaller than 35% by weight.

40 According to a preferred embodiment of the present invention, there is provided a sintered alloy in which metals of the iron family and elements of the Group 6a of periodic table including at least chromium are contained in an amount of 10 to 30% by weight with respect to the whole amount, the ratio of carbon is not greater than 0.7% by weight with respect to the whole amount, and the brightness index  $L^*$  and chromaticness indexes  $a^*$ ,  $b^*$  in the  $L^*a^*b^*$  color display system stipulated under JIS Z 8730 are  $L^* \geq 10$ ,  $a^* \leq +0.4$  and  $b^* \geq +8.0$ .

45 According to another preferred embodiment of the present invention, there is provided a sintered alloy having an average crystalline particle size of not greater than 3  $\mu\text{m}$ .

According to the present invention, metals of the iron family include nickel, iron and cobalt, elements of the Group 6a of periodic table include chromium, molybdenum and tungsten, and non-metallic elements include nitrogen, carbon etc.

50 Titanium is contained in an amount of 55 to 75% by weight with respect to the whole amount. If this amount is smaller than 55% by weight, the gold color tone becomes faint. If this amount becomes greater than 75% by weight, on the other hand, the sintering property is lost and the strength decreases. It is desired that titanium is contained in an amount of 60 to 70% by weight and, particularly, in an amount of 60 to 68% by weight. In the sintered product, titanium exists chiefly in the forms of TiN and TiCN that constitute hard phases.

55 Metals of the iron family and elements of the Group 6a of periodic table are contained in an amount of 3 to 30% by weight with respect to the whole amount. This is because, if this amount is smaller than 3% by weight, it becomes difficult to carry out the sintering and besides the sintered product loses strength. If the amount exceeds 30% by weight, on the other hand, the hardness of the sintered product is remarkably lost and the corrosion resistance is lost, too.

In order to further improve the color tone of the sintered alloy, it is desired that the metals are contained in an amount of 10 to 30% by weight and, particularly, in an amount of 12 to 23% by weight. The metals of the iron family form a binder phase in the sintered product, and elements of the Group 6a of periodic table form a hard phase or a bonding phase. Concretely speaking, it is desired that the metals of the iron family exist at a ratio of 5 to 18% by weight and the elements of the Group 6a of periodic table exist at a ratio of 3 to 12% by weight.

The ratio of carbon with respect to the non-metallic elements is selected to be not greater than 10% by weight. This is because if this ratio is greater than 10% by weight, the color tone tends to become reddish rather than the gold color, and the color changes from red copper color into greyish brown with an increase in the ratio of carbon. In order to maintain vivid and favorable gold color tone, therefore, the ratio of carbon with respect to the non-metallic elements must be selected to be not greater than 10% by weight. In particular, it is desired that the ratio of carbon with respect to the non-metallic elements is not greater than 8% by weight.

According to a particularly preferred embodiment of the present invention, the ratio of carbon is selected to be not greater than 0.7% by weight with respect to the whole amount. If this ratio is greater than 0.7% by weight with respect to the whole amount. If this ratio is greater than 0.7% by weight, the chromaticness indexes  $a^*$  and  $b^*$  become  $a^* > +0.4$  and  $b^* < +8.0$ , and the color tone tends to become reddish from its original gold color, and the color changes from red copper color into greyish brown with an increase in the ratio of carbon. In particular, the chromaticness index  $a^*$  changes with a change in the ratio of carbon. In order to maintain vivid and favorable gold color tone, therefore, the ratio of carbon must be not greater than 0.7% by weight with respect to the whole amount. In particular, it is desired that the ratio of carbon is not greater than 0.5% by weight with respect to the whole amount. In order that the amount of carbon in the sintered product is not greater than 0.7% by weight, it is recommended that the starting powder of carbide should be added in an amount as small as possible. Or, when the carbide is added in a large amount, oxides such as  $TiO_2$  and the like should be added, such that carbon in the carbide is diffused during the baking.

The ratio of chromium in the metal elements excluding titanium is larger than 35% by weight and, particularly, larger than 40% by weight. If this ratio is smaller than 35% by weight, voids easily develop in the sintered product, and dropped-out particles develop remarkably during the machining such as grinding and polishing causing the strength to decrease and the corrosion resistance to decrease, too. Further, if the ratio of chromium is smaller than 35% by weight, the brightness index  $L$  in the  $L^*a^*b^*$  color display system tends to be decreased. If the ratio of chromium with respect to the bonded metals in the sintered product is not smaller than 35% by weight, on the other hand, the sintering property is improved and the above-mentioned problems do not take place. This is attributed to that the addition of chromium improves wettability between the hard phase and the binding phase.

It is desired that the sintered alloy of gold color has an average crystalline particle size of not greater than  $8\text{ }\mu\text{m}$  and, particularly, not greater than  $3\text{ }\mu\text{m}$ . If the particle size is greater than  $8\text{ }\mu\text{m}$ , cracks develop remarkably and chipping develops during the grinding to such an extent that makes it difficult to carry out the sharp-edge machining. If the average crystalline particle size is not greater than  $3\text{ }\mu\text{m}$ , on the other hand, it is allowed to easily carry out the sharp-edge machining. This is attributed to that the ceramic material is brittle and is weak against impact and easily develops cracks. If the average crystalline particle size is not greater than  $3\text{ }\mu\text{m}$ , however, reduced stress acts upon each particle in case stress is produced by the grinding and the dropped-out particle takes place little. The remainder inevitably includes small amounts of impurities.

The sintered alloy of gold color of the present invention is obtained by mixing a nitride of titanium and a carbonitride of titanium as starting powders together with metals of the iron family and elements of the Group 6a of periodic table. The mixture is then pulverized in an organic solvent such as acetone for a predetermined period of time. Then, an organic binder is added thereto in a predetermined amount, and the mixture is molded into a desired shape by the press molding, injection molding or extrusion molding. The molded article is then placed in a non-oxidizing atmosphere heated at a temperature of  $250^\circ\text{C}$  to  $500^\circ\text{C}$  to remove the binder therefrom, followed by baking at a predetermined temperature. For instance, a nitride of titanium and a carbonitride of titanium having a particle size of  $0.5$  to  $3.0\text{ }\mu\text{m}$ , nickel and cobalt having a particle size of  $0.1$  to  $1.0\text{ }\mu\text{m}$  which are metals of the iron family, as well as chromium, WC,  $Cr_3C_2$  and  $Mo(Mo_2C)$  having a particle size of  $1.0$  to  $10.0\text{ }\mu\text{m}$  which are elements of the Group 6a of periodic table, are weighed and mixed, and are pulverized in an organic solvent such as acetone for about 20 to 100 hours and, particularly, for 48 to 72 hours. The mixture is then molded into a desired shape by the press molding, injection molding or extrusion molding. The molded article is placed in a non-oxidizing atmosphere at a predetermined temperature to remove the organic binder, followed by vacuum-baking in a vacuum heating furnace at a predetermined temperature to obtain the sintered alloy of gold color. It is desired that the vacuum-baking is carried out for 0.5 to 5 hours. Here, tungsten and chromium are added as starting carbide powders but do not stay as metallic chromium or metallic tungsten in the form of solid solution in the bonded metals, or do not stay in the form of solid solution in TiN or TiCN, or

do not exist in the form of WC or  $\text{Cr}_2\text{O}_3$  in the step of baking.

The baking is carried out at a temperature of 1300° to 1800°C in an atmosphere of a degree of vacuum of  $10^{-1}$  to  $10^{-4}$  Torr or in various atmosphere of reduced pressure or without pressure. The baking is continued for 0.5 to 5 hours though it may vary depending upon the size of the sample. After the baking, the surface of the sintered product is polished like a mirror surface using a diamond paste or the like to obtain vivid and favorable gold color with luster.

According to the present invention as described above in detail, there is obtained a sintered alloy of gold color having practically sufficient hardness and strength, excellent corrosion resistance, and mirror-like surface of elegant gold color owing to markedly improved sintering property, and which enables sharp-edge machining to be easily carried out, without permitting corrosion or scratches to develop even after used for extended periods of time. Therefore, the sintered alloy can be used for ornamental purposes such as of watch cases, watch bands, necklaces, brooches, memorial medals and buttons, and for cutlery, fishing tools and printing tools.

#### Example 1

TiN having a particle size of 2  $\mu\text{m}$ , TiCN having a particle size of 2  $\mu\text{m}$ , chromium having a particle size of 3  $\mu\text{m}$ , molybdenum having a particle size of 4  $\mu\text{m}$ , nickel having a particle size of 1  $\mu\text{m}$  and cobalt having a particle size of 1  $\mu\text{m}$  were used as starting material powders, and were weighed and mixed in a manner that the ratios of amount of the metals in the final sintered products were as shown in Table 1. The mixtures were pulverized in an organic solvent such as acetone for about 68 hours and, after paraffin was added thereto in an amount of 4 to 5% by weight, were molded Under the application of pressure of 1.5 tons/cm<sup>2</sup> into a desired shape. The molded articles were placed in a non-oxidizing atmosphere heated at a temperature of 300°C to remove the organic binder, and were then baked in vacuum in a vacuum heating furnace having a degree of vacuum of  $10^{-2}$  Torr at a temperature of 1450°C for one hour. Compositions of the thus obtained final sintered products were analyzed by the ICP emission spectroanalysis. The results were as shown in Table 1.

Table 1

Sample No.	Analytical ratio of sintered product(% by wt.)						Ratio of chromium (% by wt.)	
	Ti	Group 6a		Iron-family metal		C	N	
#1	75.3	Mo	2.7	Ni	3.0	1.2	17.8	0.0
#2	71.2	Cr	2.7	Co	1.0	0.3	20.8	35.1
				Ni	4.0			
3	70.0	Cr	4.0	Co	1.0	0.3	19.7	40.0
				Ni	5.0			
#4	69.7	Cr	3.0	Ni	6.0	0.8	19.5	30.0
				Fe	1.0			
5	68.1	Cr	4.7	Ni	6.0	0.3	19.9	40.2
		Mo	1.0					
6	68.0	Cr	5.0	Ni	7.0	0.4	19.6	41.7
7	67.5	Cr	5.0	Ni	7.5	0.2	19.8	40.0
8	65.8	Cr	7.0	Ni	7.0	0.6	19.6	50.0
#9	65.8	Cr	3.0	Ni	7.0	0.2	19.2	20.0
				Co	5.0			
#10	65.8	Cr	4.7	Co	6.0	1.3	19.0	34.3
				Fe	3.0			
11	65.8	Cr	9.5	Ni	5.0	0.5	19.2	65.6
#12	62.1	Cr	1.0	Ni	20.0	0.8	16.1	4.8
13	61.0	Cr	8.7	Ni	15.0	0.7	18.6	36.7
14	60.0	Cr	10.0	Ni	10.4	0.4	17.2	44.6
		Mo	2.0					
15	55.7	Cr	9.8	Ni	18.0	0.6	15.9	35.3
#16	54.7	Cr	7.3	Ni	20.0	0.9	17.1	26.7
#17	53.5	Cr	15.0	Ni	15.0	0.8	15.7	50.0

Samples marked with # lie outside the scope of the invention.

The surfaces of the sintered products were ground and polished like a mirror. The samples were then tested for their color tone, bending strength, Vickers' hardness (Hv), anti-chipping property and corrosion resistance. The bending strength was measured in accordance with the three-point bending test stipulated under JIS R 1601, the Vickers' hardness was measured in compliance with the testing method of JIS Z 2244, and the anti-corrosion testing was carried out by using human sweat (pH 4.7) in compliance with the standards of the ISO (International Standardization Organization) as a corrosive solution, immersing the lower half of the mirror surface-polished sample in the human sweat maintained at 40°C + 2°C for 24 hours, and the conditions of the

polished surfaces of the samples after immersed were observed. The color tone was measured and evaluated by using an L\*a\*b\* optical color difference meter (manufactured by Minolta Co.), i.e., by using a high-functional-color color difference meter (in compliance with JIS Z 8722) of the 45° ring illumination vertical light-receiving system. The anti-chipping property was evaluated in terms of a maximum chipping width of when the mirror surface-polished sample was creep-ground. The results were as shown in Table 2 and 3.

Table 2

Sample No.	Color difference		
	L <sup>*</sup> (Brightness)	a <sup>*</sup> (+red, -green)	b <sup>*</sup> (+yellow, -blue)
#1	4.2	+0.8	+27.4
#2	9.0	-0.4	+18.1
3	24.0	-0.3	+15.0
#4	18.2	+0.6	+12.4
5	20.4	-0.4	+16.2
6	39.0	-0.1	+12.6
7	33.8	-2.0	+13.7
8	40.0	+0.2	+11.8
#9	8.9	-2.0	+9.4
#10	8.1	+1.3	+9.6
11	45.1	-0.6	+9.9
#12	7.0	+0.6	+5.2
13	12.4	+0.4	+8.0
14	34.3	-0.2	+8.4
15	30.5	+0.1	+8.0
#16	10.8	+0.5	+7.2
#17	21.5	+0.6	+3.8

The samples marked with # lie outside the scope of the invention.

Table 3

	Sample No.	Deflective strength (kg/mm <sup>2</sup> )	Vickers' hardness	Corrosion resistance	Anti-chipping property	Color tone	remarks
5	#1	30	1500	△	○	—	poorly sintered
10	#2	55	1250	○	○	—	poor mirror surface
	3	90	1380	○	○	gold color	
15	#4	90	1050	○	△	orange	
	5	95	1350	○	○	gold color	
	6	120	1150	○	○	gold color	
20	7	105	1050	○	○	gold color	
	8	115	1100	○	○	gold color	
25	#9	105	1050	△	△	—	poor mirror surface
	#10	90	1000	△	X	reddish gold color	
30	11	125	1050	○	○	gold color	
	#12	50	940	X	X	—	poorly sintered
	13	135	1050	○	○	gold color	
35	14	115	1100	○	○	gold color	
	15	140	980	○	○	gold color	
40	#16	70	850	X	○	orange	
	#17	120	970	△	○	reddish white	

Samples marked with # lie outside the scope of the invention.

45 Sample numbers indexed with marks in Tables 1, 2 and 3 indicate being outside of the invention. As to the results of anticorrosion tests circle mark ○ represent no discoloration, triangular mark △ represents discoloration and cross mark X represents discoloration and corrosion. As to the antichipping property, circle mark ○ indicate good for sharp edge working, triangular mark △ indicates not suitable for sharp edge working as sporadic chippings in sizes of 1 to 5 μm appear and cross mark X indicates unfit for sharp edge working as chippings in sizes of larger than 5 μm occur in a great number.

50 It will be understood from the above Tables 1, 2 and 3 that the samples that lie within the scope of the present invention have very excellent bending strength, Vickers' hardness, corrosion resistance and anti-chipping property, and exhibit elegant gold color.

#### 55 Example 2

TiN having a particle size of 1.2 μm, TiCN having a particle size of 1.5 μm, Cr<sub>3</sub>C<sub>2</sub> having a particle size of 7.0 μm, WC having a particle size of 9.0 μm, nickel having a particle size of 3.0 μm, and cobalt having a particle

size of 4.0  $\mu\text{m}$  were used as starting material powders, and were weighed and mixed in a manner that the ratios of amounts of the metals in the final sintered products were as shown in Table 1. The mixtures were pulverized in an organic solvent such as acetone for about 68 hours and, after paraffin was added thereto in an amount of 4 to 5% by weight, were molded under the application of pressure of 1.5 tons/cm<sup>2</sup> into a desired shape. The molded articles were placed in a non-oxidizing atmosphere heated at a predetermined temperature to remove the organic binder, and were then baked in vacuum in a vacuum heating furnace having a degree of vacuum of  $10^{-2}$  Torr at a temperature of 1450°C for one hour. The thus obtained final sintered products were analyzed by the ICP emission spectroanalysis. The results were as shown in Table 4.

Table 4

Sample No.	Analytical ratio of sintered product (% by weight)						C/C+N (wt%)	Ratio of chromium (wt%)
	Ti	Group 6a	Iron-family metal		C	N		
#1	75.8	Cr 0.9	Ni	1.0	0.1	22.2	0.4	47.4
2	74.5	Cr 2.0	Ni	1.4	0.3	21.8	1.4	58.8
3	69.6	Cr 4.3 W 1.5	Ni	3.5	0.8	20.3	3.8	46.2
4	68.1	Cr 5.0	Ni	7.0	1.0	18.9	5.0	41.7
5	67.7	Cr 5.0	Ni	7.5	0	19.8	0	40.0
6	65.8	Cr 6.5	Ni	7.5	1.0	19.2	5.0	46.4
7	58.0	Cr 10.7	Ni	5.0	0	19.2	0	66.7
#8	58.0	Cr 8.7	Ni	15.0	1.3	17.0	7.1	36.7
9	58.0	Cr 10.4	Ni 10.0 Co 3.0		1.6	17.0	8.6	44.4
#10	56.5	Cr 13.0	Ni	12.0	2.0	16.5	10.8	52.0
#11	54.0	Cr 14.5	Ni 9.5 Co 4.0		2.2	15.8	12.2	51.8
#12	50.3	Cr 21.7	Ni	10.0	3.3	14.7	18.3	68.5

Samples marked # lie outside the scope of the invention.

The surfaces of the sintered products were ground and polished like a mirror. The samples were then tested for their color tone, bending strength, Vickers' hardness (Hv), porosity, average crystalline size, anti-chipping property and corrosion resistance. The bending strength was measured in accordance with the three-point bending test stipulated under JIS R 1601, the Vickers' hardness was measured in compliance with the testing method of JIS Z 2244, and the porosity was measured according to the Archimedes' method. The anti-corrosion testing was carried out by using human sweat (pH 4.7) in compliance with the standards of the ISO (International Standardization Organization) as a corrosive solution, immersing the lower half of the mirror surface-polished sample in the human sweat maintained at 40°C  $\pm$  2°C for 24 hours, and the conditions of the polished surfaces of the samples after immersed were observed. The average crystalline particle size was calculated from an S.E.M photograph of the sintered product. The anti-chipping property was indicated in terms of a max-



imum chipping width of when the mirror surface-polished sample was creep-ground. The results were as shown in Table 5.

Table 5

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Sample No.	Average particle diameter ( $\mu\text{m}$ )	Porosity	Deflective strength ( $\text{kg}/\text{mm}^2$ )	Vickers' hardness Hv ( $\text{kg}/\text{mm}^2$ )	Corrosion resistance	Anti-chipping property	Color tone
#1	2.5	X	—	—	—	X	poorly sintered
2	2.8	○	90	1600	○	○	gold color
3	1.3	○	110	1400	○	○	gold color
4	1.5	○	150	1300	○	○	gold color
5	1.8	○	125	1350	○	○	gold color
6	2.3	○	125	1350	○	○	gold color
7	2.3	○	115	1400	○	○	gold color
#8	1.8	○	120	1150	X	○	gold color
9	2.2	○	140	1150	○	○	gold color
#10	2.5	○	140	1200	○	○	reddish golden color
#11	3.3	○	130	950	○	X	dark gold color
#12	3.5	○	135	1050	○	X	red copper color

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The samples marked with # lie outside the scope of the invention.

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In Tables 4 and 5, the samples marked with # lie outside the scope of the present invention. Concerning the porosity in Table 5, furthermore, an open circle ○ represents high-density products with the porosity of smaller than 5% and a mark X represents low-density products with the porosity of greater than 5%. As for the anti-corrosion testing, an open circle ○ represents the products without any discoloration or corrosion, and a mark X represents the products that were discolored and corroded. As for the anti-chipping property, an open circle ○ represents the products that could be favorably sharp-edge machined, and a mark X represents the products that developed chipping and could not be sharp-edge machined.

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It will be understood from the above Tables 4 and 5 that the samples Nos. 2 to 7 and 9 that lie within the scope of the present invention have very excellent porosity, bending strength, Vickers' hardness, corrosion resistance and anti-chipping property, and exhibit elegant gold color.

### Claims

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1. A sintered alloy of gold color comprising a nitride of titanium or a carbonitride of titanium and metals, wherein titanium is contained in an amount of 55 to 75% by weight with respect to the whole amount, metals of the iron family and elements of the Group 6a of periodic table including at least chromium are contained in an amount of 3 to 30% by weight with respect to the whole amount, and the remainder being non-metallic

elements consisting of nitrogen or nitrogen and carbon, and wherein the ratio of carbon with respect to said non-metallic elements is not greater than 10% by weight, and the ratio of chromium in the metal elements excluding titanium is not smaller than 35% by weight.

- 5 2. A sintered alloy of gold color according to claim 1, wherein metals of the iron family and elements of the Group 6a of periodic table including at least chromium are contained in an amount of 10 to 30% by weight with respect to the whole amount, the ratio of carbon is not greater than 0.7% by weight with respect to the whole amount, and the brightness index  $L^*$  and chromaticness indexes  $a^*$ ,  $b^*$  in the  $L^*a^*b^*$  color display system stipulated under JIS Z 8730 are  $L^* \geq 10$ ,  $a^* \leq +0.4$  and  $b^* \geq +8.0$ .
- 10 3. A sintered alloy of gold color according to claim 2, wherein titanium exists in an amount of 60 to 68% by weight with respect to the whole amount.
4. A sintered alloy of gold color according to claim 2, wherein metals of the iron family and elements of the Group 6a of periodic table exist in amounts of 12 to 23% by weight with respect to the whole amount.
- 15 5. A sintered alloy of gold color according to claim 2, wherein metals of the iron family exist at a ratio of 5 to 18% by weight and elements of the Group 6a of periodic table exist at a ratio of 3 to 12% by weight with respect to the whole amount.
- 20 6. A sintered alloy of gold color according to claim 1, wherein the sintered alloy has a average crystalline particle size which is not greater than 3  $\mu\text{m}$ .
7. A sintered alloy of gold color according to claim 6, wherein the ratio of chromium in the metal elements excluding titanium is not smaller than 40% by weight.
- 25 8. A sintered alloy of gold color according to claim 6, wherein titanium exists in an amount of 60 to 70% by weight with respect to the whole amount.
9. A sintered alloy of gold color according to claim 6, wherein the ratio of carbon with respect to the non-metallic elements is not greater than 8% by weight.
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European Patent  
Office

# EUROPEAN SEARCH REPORT

Application Number

DOCUMENTS CONSIDERED TO BE RELEVANT			EP 92110770.2
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. CL.5)
A	US - A - 4 589 917 (NAGATO) * Claims *	1	C 22 C 29/16
D,A	CHEMICAL ABSTRACTS, vol. 99, no. 14, October 03, 1983, Columbus, Ohio, USA TOSHIBA TUNGALOY CO. "Ornamental golden-colored titanium monoxide-base composites" page 252, column 2, abstract-no. 109 451t & Jpn. Kokai Tokkyo Koho JP 58 91,145	1	
A	CHEMICAL ABSTRACTS, vol. 95, no. 2, July 13, 1981, Columbus, Ohio, USA MITSUBISHI METAL CORP. "Ornamental hard sintered alloys" page 250, column 2, abstract-no. 11 128k & Jpn. Kokai Tokkyo Koho 81 09,352	1	TECHNICAL FIELDS SEARCHED (Int. CL.5)  C 22 C
A	CHEMICAL ABSTRACTS, vol. 80, no. 16, April 22, 1974, Columbus, Ohio, USA YONEYA KATSUTOSHI et al. "Hard alloy for ornament" page 233, column 2, abstract-no. 86 547c & Japan. Kokai 73 94,607	1	
The present search report has been drawn up for all claims			
Place of search VIENNA		Date of completion of the search 22-09-1992	Examiner LUX
<p><b>CATEGORY OF CITED DOCUMENTS</b></p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons &amp; : member of the same patent family, corresponding document</p>			

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